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Movement of Contaminants from Oily Wastes during Land Treatment

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by

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16. ABSTRACT

Land treatment is a method of handling wastes that are used by the petroleum refinery industry and others. This method allows the simultaneous treatment and final disposal of the wastes. The soil properties and biota are depended upon to degrade, transform or immobilize the hazardous constituents of the wastes.

A mathematical model of the land treatment process has been developed which will simulate the movement of contaminants as oily wastes are degraded. The model examines the fate of these constituents in the soil, oil, water and air phases of the treatment system. The model assumes no dispersion, local equilibrium, linear partitioning of the contaminant between phases, volatile losses by a modified Thibodeaux-Hwang approach, first-order degradation kinetics, no migration of oil after application, a uniform soil profile, and constant water flux throughout the treatment zone.

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INTRODUCTION

The purpose of this paper is to describe a mathematical model which analyzes the fate of hazardous constituents during the land treatment of oily wastes. This model considers biological degradation, deep percolation, and volatilization. One feature of the model is a prediction of the effect that the presence of oil has on the movement of contaminants.

LAND TREATMENT - EFFECTIVE AND ECONOMICAL

Land treatment is a method of handling hazardous wastes that consists of the simultaneous treatment and final disposal of the waste. The waste is incorporated into the upper zone of the soil which serves as a treatment medium for organics and a repository for inorganics. The application levels of the wastes are strictly controlled, and continuous management and monitoring are a necessity. Systems are designed and operated to optimize utilization of natural biological, chemical, and physical soil processes and interactions for the purpose of achieving degradation, transformation, and/or immobilization of hazardous constituents. Successful treatment of hazardous waste can be achieved only if soil conditions are maintained that maximize these mechanisms of treatment. Properly designed and managed facilities are capable of accomplishing this disposal without the contamination of surface waters, ground water, or atmosphere.

Land treatment, obviously is not the answer to all waste residual management problems. As with every other alternative, it has its limitations. Even so, under the proper circumstances, land treatment can offer a very efficient and economical disposal option which deserves consideration.

Land treatment as a disposal technology has been practiced for centuries around the world. Historically, this practice has been used primarily for treating low volumes of domestic and agricultural wastes. Currently, this mode of treatment is now considered not only as a cost-effective method of disposal for much larger volumes of agricultural and domestic wastewaters and residuals, but also for such complex waste residuals as those generated by the petroleum refinery and petrochemical industries.

The petroleum refinery industry has been land-treating selected refinery wastes for 30 years and is presently the predominant industry utilizing this treatment technology. It is the most attractive technology available for disposing of oily sludges and is incurring rapid growth. The number of industrial treatment systems being built has shown a significant increase in recent years. A wide diversity of industrial categories are currently operating full- or pilot-land treatment systems. These include: petroleum refining, food processing, textiles, pulp and paper, metal plating, leather tanning, printing ink, paint, munitions, foundries, inorganic chemicals, organic chemicals and pharmaceuticals. The popularity of land treatment seems destined to grow as industries strive to find more efficient, cost-effective methods of hazardous waste management.

MATHEMATICAL MODEL

Expanding the application of land treatment technology in an orderly and environmentally acceptable manner will require an understanding of the various processes that occur in the treatment zone as well as the interactions of each process. One tool that could be useful to such an understanding and application of land treatment technology is mathematical modeling of the treatment zone.

Land Treatment Processes

Figure 1 presents a schematic view of the major processes that can occur in any land treatment system. The treatment zone is the area of the soil profile where treatment occurs and is defined by regulations such that its depth is no more than 1.5 meters. As shown, the treatment zone consists of two regions: the plow zone and the lower treatment zone. Within the plow zone (0-0.3 meters) the oily sludge is applied and tilled into the soil. The reasons for tilling are several: it helps oxygenate the treatment zone, it reduces volatile emissions, it spreads the waste out in the soil so that they are more dilute and can be better utilized by the soil biological population, and it brings the waste into intimate contact with the soil bacteria. Sometimes, commercial fertilizers are added to the plow zone to improve the carbon to nitrogen to phosphorous ratio for the microbiological population.

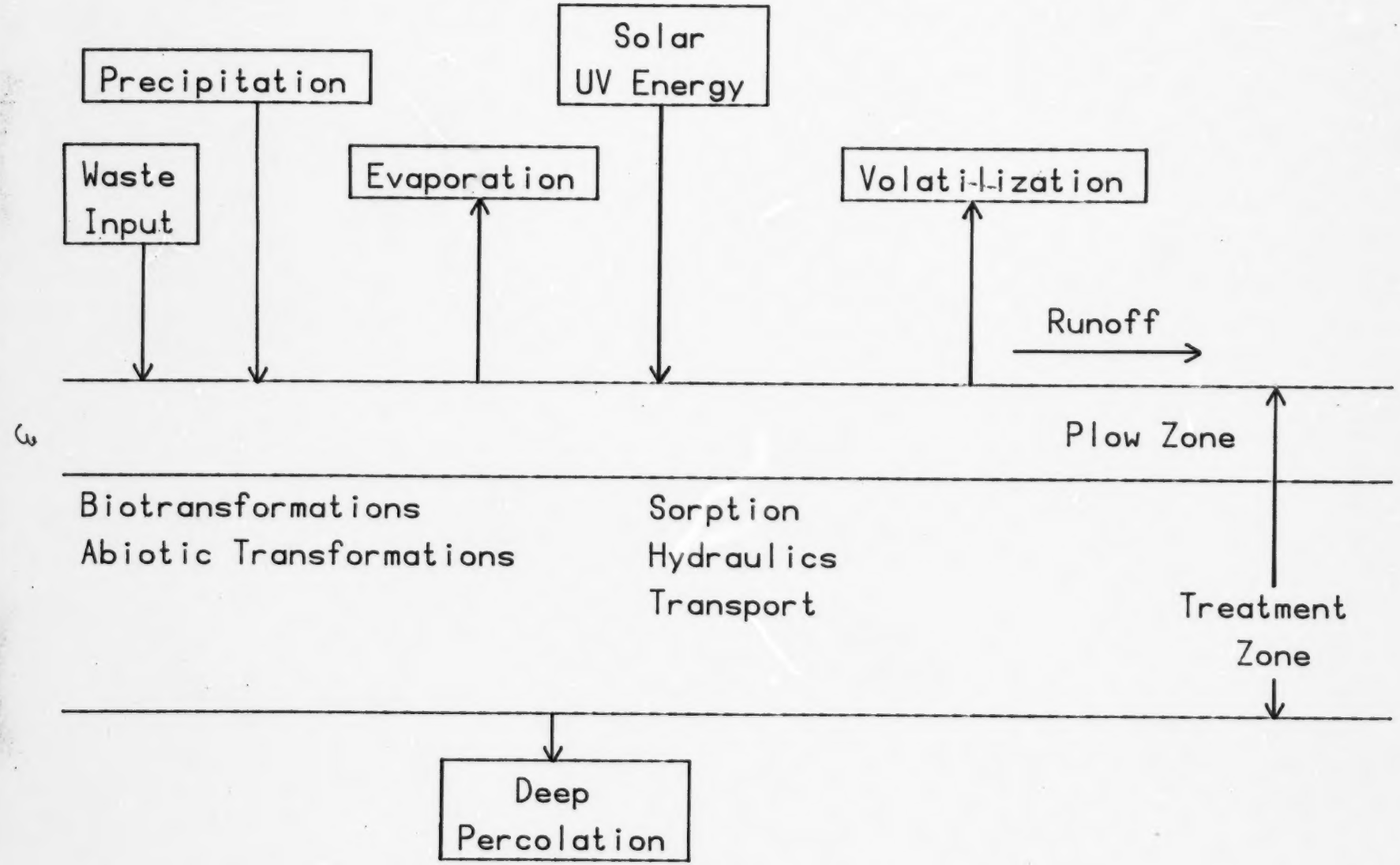

Fig. 1. Land Treatment Processes

Rainfall on the soil provides needed moisture for the biological population in the treatment zone. However, excess rainfall can cause problems with runoff and deep percolation. Of course, some of the water from rainfall will also evaporate. Another concern is volatile losses of hazardous constituents from the treatment zone to the atmosphere. UV energy from sunlight can promote the photooxidation of volatilized constituents and organics near the surface.

Within the plow zone and treatment zone several processes can occur which will affect the migration of constituents. Organic components are subject to biotransformation. Ideally hazardous materials are transformed into carbon dioxide and water. However, in some cases it is adequate to transform them into other organics which are nontoxic. Abiotic transformations such as precipitation of inorganics or hydrolysis of organics can occur. Sorption of the hazardous materials by the soil is also important. Sorption retards migration so that constituents remain within the treatment zone for a longer period of time. Thus they become subject to a higher degree of degradation.

Hydraulics provide the major means of transport of constituents through the treatment zone to groundwater by leaching. Basically, land treatment can be regarded as a race between migration and degradation. If degradation can reduce the concentration of the material before it migrates out of the treatment zone then land treatment will be successful.

Assumptions

In a previous paper, Short (1985) examined the application of the transport equations in modeling of the hazardous waste land treatment process. The current model uses these results with several simplifying assumptions.

It is first assumed that dispersion is insignificant and can be neglected. A plug flow or kinematic model will thus result. The assumption of local equilibrium is also made. Normally the transport of constituents between each of the phases (soil, water, air, and oil) is rapid in comparison to the bulk flow of water through the soil. Also linear equations (linear isotherm, Henry's law, and linear oil-water partitioning) are used to describe the distribution of constituents between phases. Losses of volatile constituents by vaporization are represented by a modified Thibodeaux-Hwang (1982) approach, see Short (1985). First-order degradation kinetics are assumed to apply to all constituents in the waste including oil that may be present. It is also assumed that any oil in the waste will not migrate once it is applied. Uniform soil characteristics throughout the entire treatment zone are assumed. A constant water flux through the treatment zone is assumed. Finally, it is assumed that the waste is applied uniformly and is evenly distributed through the plow zone.

Plow Zone Material Balance

In order to develop a model for a land treatment process, we first divide the treatment zone into two sections, the plow zone and the lower treatment zone. A material is performed around the plow zone so that the amount of constituent that leaches into the lower treatment zone can be evaluated. This material balance is illustrated in Figure 2. The use of the assumptions previously described, yields a situation shown in this figure. The constituent of interest, at a given time, will be located at depths of X_D or greater. At the beginning or time equal to zero, the constituent slug will be located at depths from the soil surface to the bottom of the plow zone. Because of volatilization and leaching, the constituent slug will move downward creating a "dry" zone which does not have any constituent. As time goes on, the location of X_D increases until it finally moves out of the plow zone into the lower treatment zone. This movement is illustrated in Figure 3. It must be kept in mind that volatile constituents are allowed to diffuse through the "dry" zone to the soil surface. Also the concentration in the pollutant slug will decrease with time due to degradation.

Thus the material balance for a given constituent can be expressed as follows: The sum of the amount volatilized, the amount leached out of the plow zone, the amount degraded, and the amount remaining in the plow zone is equal to the amount that was applied to the surface.

Concentration and Phase Partitioning

Because of the boundary conditions associated with land treatment, it is convenient to utilize the total concentration and phase relationships recommended by Jury, et al. (1983). The total concentration can be expressed as a sum of the contributions from each phase as:

$$C_T = \rho C_S + \theta C_A + \eta C_V + \phi C_O \qquad (1)$$

where C_T = mass of constituent per soil volume (gm/M^3)
θ = volumetric water content of the soil (M^3/M^3)
ϕ = volumetric oil content of soil (M^3/M^3)
η = volumetric air content of the soil (M^3/M^3)
ρ = bulk density of the soil (Kg/M^3)
C_A = aqueous solution concentration (gm/M^3)
C_O = oil phase concentration (gm/M^3)
C_V = vapor concentration (gm/M^3)
C_S = adsorbed concentration (gm/Kg soil)

To describe the partitioning of the pollutant between the soil and the aqueous phase, we assume a linear isotherm. This yields a simple linear relationship for solid-liquid partitioning.

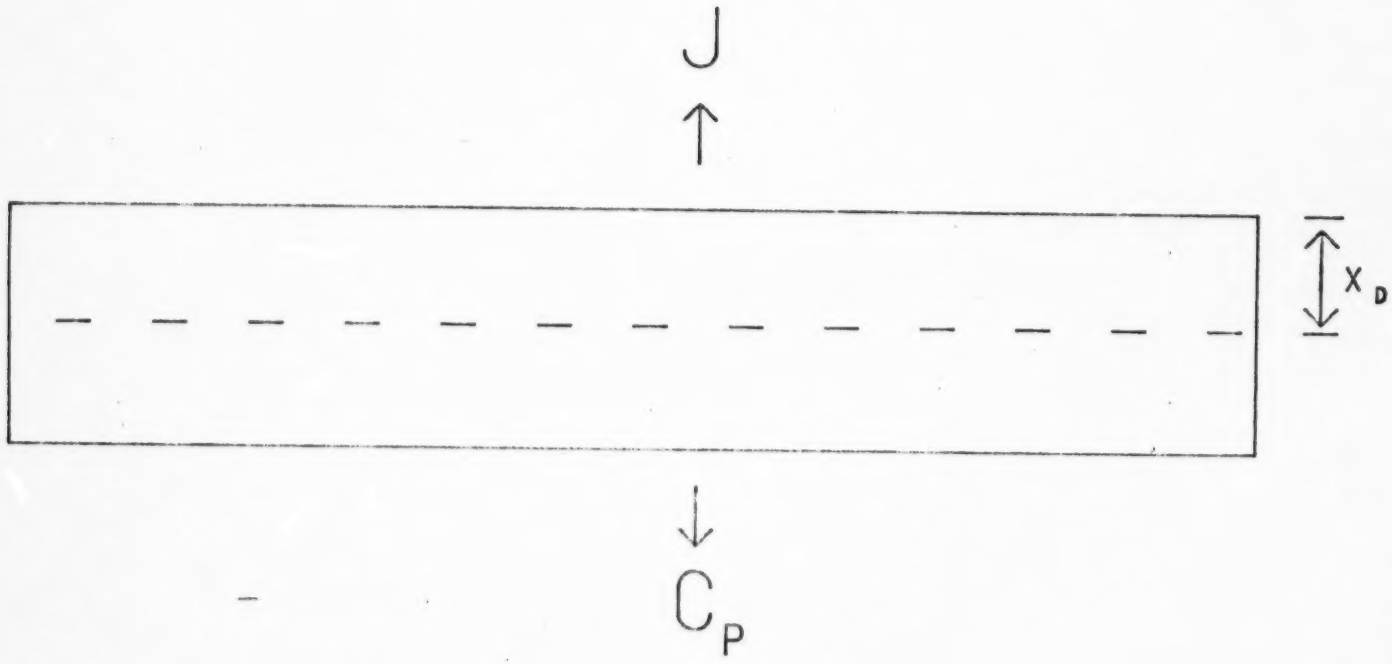

Fig. 2. Plow Zone Material Balance

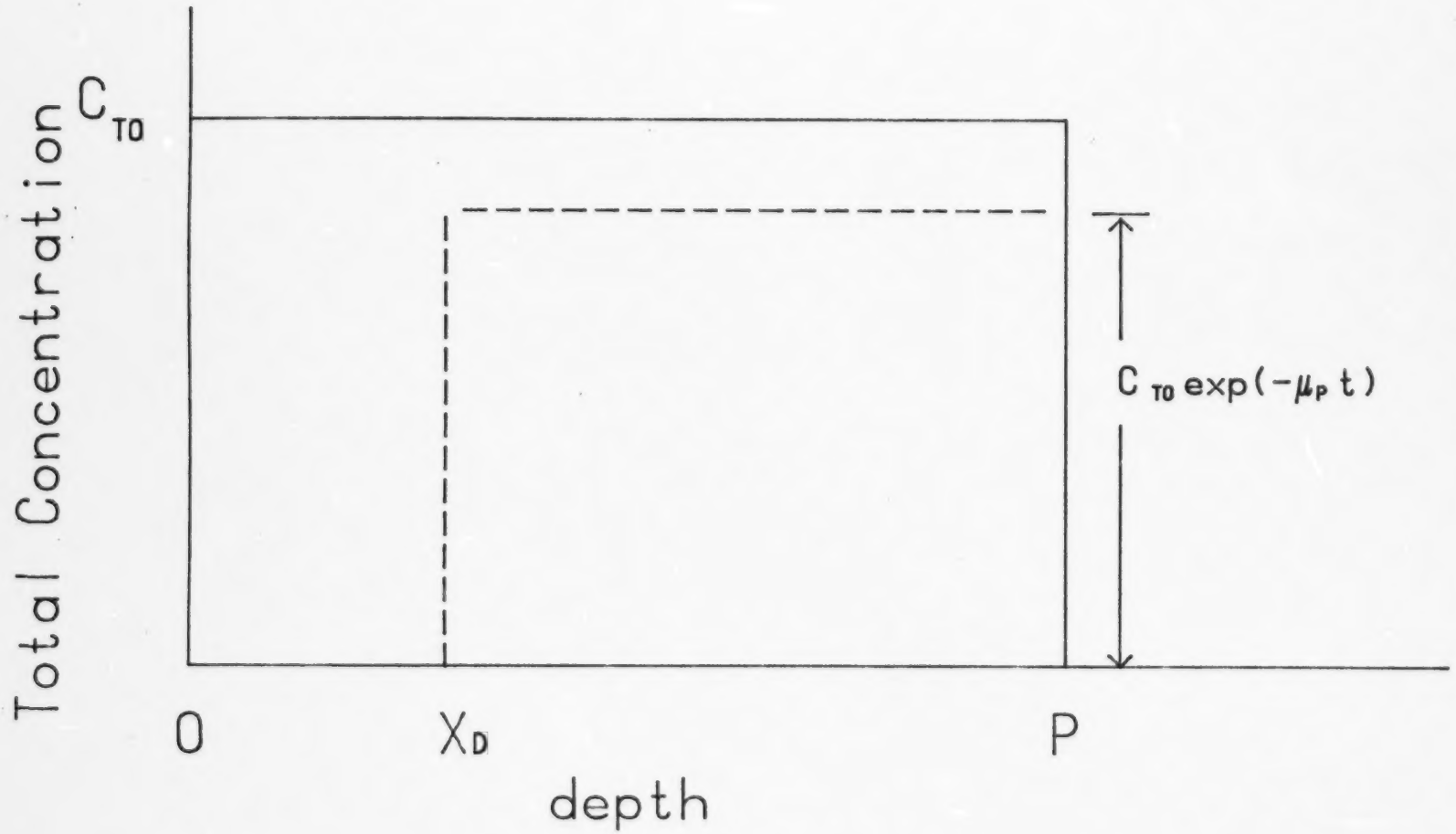

Fig. 3. Plow-Zone Transport

$$C_S = K_D C_A \tag{2}$$

where K_D = linear isotherm constant (M^3/Kg)

Partitioning of the pollutant between the aqueous and vapor phase is generally represented by Henry's Law.

$$C_V = K_H C_A \tag{3}$$

where K_H = Henry's law constant (dimensionless)

In order to describe the partitioning between the oil and aqueous phases, we assume a simple linear partitioning relationship.

$$C_O = K_O C_A \tag{4}$$

where K_O = linear oil/water partition constant (dimensionless)

Under the assumption of local equilibrium, equations (2), (3), and (4) are sufficient to completely describe the distribution of the pollutant among the aqueous, oil, vapor, and solid phases. Using equation (1) and these linear approximations, we can write an expression for the total concentration in terms of the individual phase concentrations.

$$C_T = B_A C_A = B_S C_S = B_O C_O = B_V C_V \tag{5}$$

where $B_A = \rho K_D + \theta + \eta K_H + \phi K_O$ (6)

$B_S = B_A/K_D$ (7)

$B_O = B_A/K_O$ (8)

$B_V = B_A/K_H$ (9)

For convenience the following retardation factor is defined:

$$R = (\rho K + \theta + \eta K_H)/\theta \tag{10}$$

Also we define the following factor which represents the contribution of the oil phase sorption to the overall retardation factor.

$$R_O = (\phi K_O)/\theta \tag{11}$$

Thus

$$B_A = (R + R_O)\theta \tag{12}$$

Plow Zone Leachate Concentration

Using the definition of total concentration along with the linear phase relationships, an expression can be developed for the plow zone leachate concentration. First-order degradation

kinetics is used for the degradation of the oil and pollutant. Thus:

$$C_p = \frac{C_{TO}\exp(-\mu_p t)}{\theta[R + R_T\exp(-\mu_0 t)]} \tag{13}$$

where $R_T = \phi_0 K_0/\theta$ (14)

ϕ_0 = oil content at initial time (M^3/M^3)
C_{TO} = initial total concentration in the plow zone (gm/M^3)
C_p = leachate concentration from the plow zone (gm/M^3)
μ_P = first-order degradation constant for the pollutant (1/day)
μ_0 = first-order degradation constant for oil (1/day)
t = time (day)

The oil phase can act as an large sink for pollutants. This is particularly true for hydrophobic compounds. The oil acts so as to retard the migration of these compounds. Depending upon the relative degradation rates, it is possible for the oil to release pollutant into the other phases as it degrades. If the degradation rate of the oil is faster than that of the pollutant, an increase of pollutant concentration in the leachate is predicted by equation (13) for a short period of time.

This expression for the leachate concentration can be used to determine amount of pollutant leached from plow zone with the expression below.

$$\text{amount leached} = \int_0^t C_p\, V_{A0}\, dt \tag{15}$$

where V_A = interstitial aqueous velocity (M/day)

Volatilization

Thibodeaux and Hwang (1982) have suggested a model for the volatile emissions from land treatment. Their approach was based upon their concept of a "wet/dry" zone. This concept is illustrated in Figure 4. In this approach it is assumed that initially the soil is contaminated to the depth of the plow zone. As the pollutant volatilizes, the vapors diffuse through the pores upward to the surface. There quickly develops a "dry" zone. Just below this is a "wet" zone that contains all of the contamination. The concentration in the wet zone is unaffected by volatilization. Only the location of the "wet/dry" zone interface is altered by the process of volatilization. Their approach is modified in this paper by adding the resistance to diffusion of a stagnant layer of air above the surface of the soil. The assumed thickness of this layer is δ. Thus the diffusional flux of the contaminant can be expressed as:

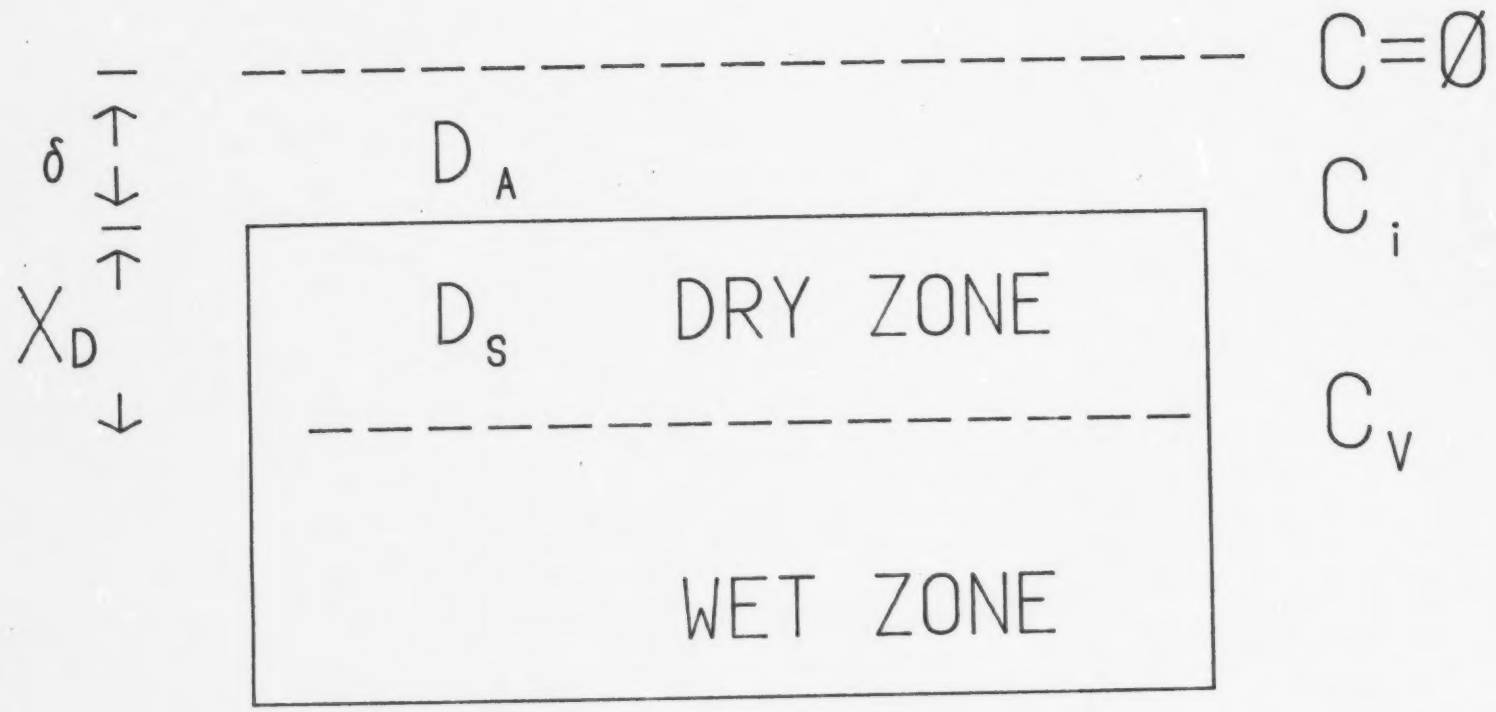

Fig. 4. Modified Thibodeaux-Hwang Volatilization Model

$$J = \frac{C_V D_S D_S}{D_S \delta + D_A X_D} \tag{16}$$

where J = mass flux of the pollutant through the vapor phase (gm/M^2-day)

D_A = vapor diffusion coefficient of pollutant in air (M^2/day)

D_S = effective vapor diffusion coefficient of the pollutant through the soil pores (M^2/day)

δ = boundary layer thickness of the stagnant layer of air above the soil (M)

The effective diffusion coefficient is usually determined by multiplying the diffusion coefficient of the pollutant in air by a tortuosity factor which accounts for the increased diffusion path and lowered surface area that occurs in soil pores. One such correction factor is determined from the model of Millington-Quirk (1961). With this model the correction factor is shown below:

$$D = \left[\frac{\eta^{10/3}}{\rho^2}\right] D_A \tag{17}$$

Jury, et al. (1983) has recommended the following expression to estimate the thickness of the stagnant layer of air.

$$\delta = \frac{D_W \rho_{WV} (1-RH)}{2 E \rho_{WL}} \tag{18}$$

where D_W = the diffusion coefficient of water vapor in air (M^3/day)

ρ_{WL} = liquid water density (gm/M^3)

RH = relative humidity (fraction)

E = evaporation rate (M/day)

ρ_{WV} = water vapor density (gm/M^3)

This expression was developed by assuming that the evaporation rate and the volatilization flux are controlled by the same stagnant layer. It also assumed that the evaporation is negligible at night. Thus the steady state evaporation rate is equal to one-half of the total evaporation rate. Now we can express for the plow zone mass balance the amount volatilized.

$$\text{amount volatilized} = \int_0^t J dt \tag{19}$$

Accumulation of pollutant in plow zone

The term in the plow zone mass balance, which is called accumulation, equals the materials which remain within the plow zone. With no dispersion and the volatilization concept of Thibodeaux-Hwang (1982), the concentration of the pollutant in the "wet" zone does not change because of either volatilization or leaching. The change of concentration is due only to degradation which is assumed to follow first-order kinetics. Thus accumulation can be expressed as a function of the "wet/dry" zone interface depth and time for degradation as shown below:

$$\text{accumulation} = (P-X_D)C_{TO}\exp(-\mu_p t) \tag{20}$$

where P = depth of the plow zone (M)
X_D = depth to the top of the pollutant slug (M)

Application

The amount of pollutant applied to the plow zone can be expressed in terms of the initial plow zone concentration as follows:

$$\text{amount applied} = C_{TO}P \tag{21}$$

Degradation

The amount degraded can be expressed in terms of the accumulated amount of the pollutant times the reaction rate constant as follows:

$$\text{degradation} = \int_0^t (P-X_D)C_{TO}\exp(-\mu_p t)\mu_p dt \tag{22}$$

Equations (19), (20), (21), and (22) can be used to write a material balance around the plow zone. If this equation is differentiated and rearranged, the following can be derived:

$$\frac{dX}{dt} = \frac{A\,V_A}{[R+R_T\exp(-\mu_0 t)](D_S\delta + D_A X_D)} + \frac{V_A}{R + R_T\exp(-\mu_0 t)} \tag{23}$$

$$\text{where } A = \frac{K_H D_S D_A}{V_A \vartheta} \tag{24}$$

Equation (23) is the defining equation that describes the position of the "wet/dry" zone interface for a land treatment system. This equation computes the rate of change or the interface as the sum of two terms. The first term gives the contribution of volatilization to its velocity of the interface. The second term gives the contribution of leaching/retardation to the interface velocity.

This differential equation can be solved by simple integration using the initial condition that the location of the interface is at the surface (depth equals zero) at time equal zero. This solution is shown below:

$$X_D - \left[\frac{A}{D_A}\right] \ln\left[1 + \frac{X_D}{G}\right] = \frac{V_A}{R}\left\{t + \frac{1}{\mu_o} \ln\left[\frac{R + R_T \exp(-\mu_o t)}{R + R_T}\right]\right\} \quad (25)$$

where $$G = \frac{A}{D_A} + \frac{D_S}{D_A} \quad (26)$$

Equation (25) can be solved by trial and error procedures to determine the location of the interface as a function of time. Once the interface position is determined, then all of the mass balance terms such as volatilization flux, accumulation, etc. can be computed. Thus the fate of pollutants in the plow zone can be defined.

Lower Treatment Zone Material Balance

With a complete description of the fate of pollutants in the plow zone, we can now proceed to evaluate their fate in the lower portion of the treatment zone. This is done by completing a mass balance similar to that done for the plow zone.

For the lower treatment zone, the input of pollutant is the leachate from the plow zone. Volatilization from the lower treatment zone is neglected until the location of the "wet/dry" zone interface moves from the plow zone into the lower treatment zone. We assumed that oil does not migrate into the lower treatment zone. Thus the retardation coefficient in this portion of the treatment zone is constant. Therefore, the velocity of a pollutant slug can be computed directly. We also assume that degradation continues to take place at the same rate as occurs in the plow zone.

The material balance in the lower treatment zone can be written assuming a semi-infinite soil column, thus a leachate term does not have to be included in the overall material balance.

Lower Treatment Zone Input

The input to the lower treatment zone can be expressed as the integral of the plow zone leachate times the aqueous flow velocity.

$$\int_0^{t<t_{BRK}} V_A \theta C_p dt = \int_0^{t<t_{BRK}} \frac{V_A C_{TO} \exp(-\mu_p t) dt}{[R + R_T \exp(-\mu_0 t)]} \qquad (27)$$

Note that the upper limit of integration is restricted to times less than the length of time it takes for the location of the "wet/dry" zone interface to leave the plow zone. This is because after that time, the input falls to zero. Figure 5 illustrates a slug of pollutant moving from the plow zone to the lower treatment zone.

Accumulation in Lower Treatment Zone

To determine the amount of accumulation of pollutant in the lower treatment zone, we consider a small element of soil located immediately below the plow zone as is shown in Figure 6. The aqueous phase concentration is equal to the plow zone leachate concentration. At some increment of time we allow this element to move at the same velocity as that of a pollutant slug. The aqueous phase concentration is now reduced by an amount that can be determined by the application of first-order kinetics. We can compute the total concentration in the element by applying linear partitioning. Recognizing that the oil content is zero in the lower treatment zone, the amount accumulated can now be determined by integrating the total concentration over the length of the pollutant slug. The results of this integration is shown in equation (28). The bottom of the pollutant slug can be determined from the pollutant velocity as is shown in equation (29).

$$\int_{X_D}^{X_B} C_T dX = C_{TO} \exp(-\mu_p t)$$

$$\left\{ (X_B - X_D) + \frac{V_p}{\mu_0} \ln \left[\frac{R + R_T \exp[-\mu_0 (X_B - X_D)/V_p]}{R + R_T} \right] \right\} \qquad (28)$$

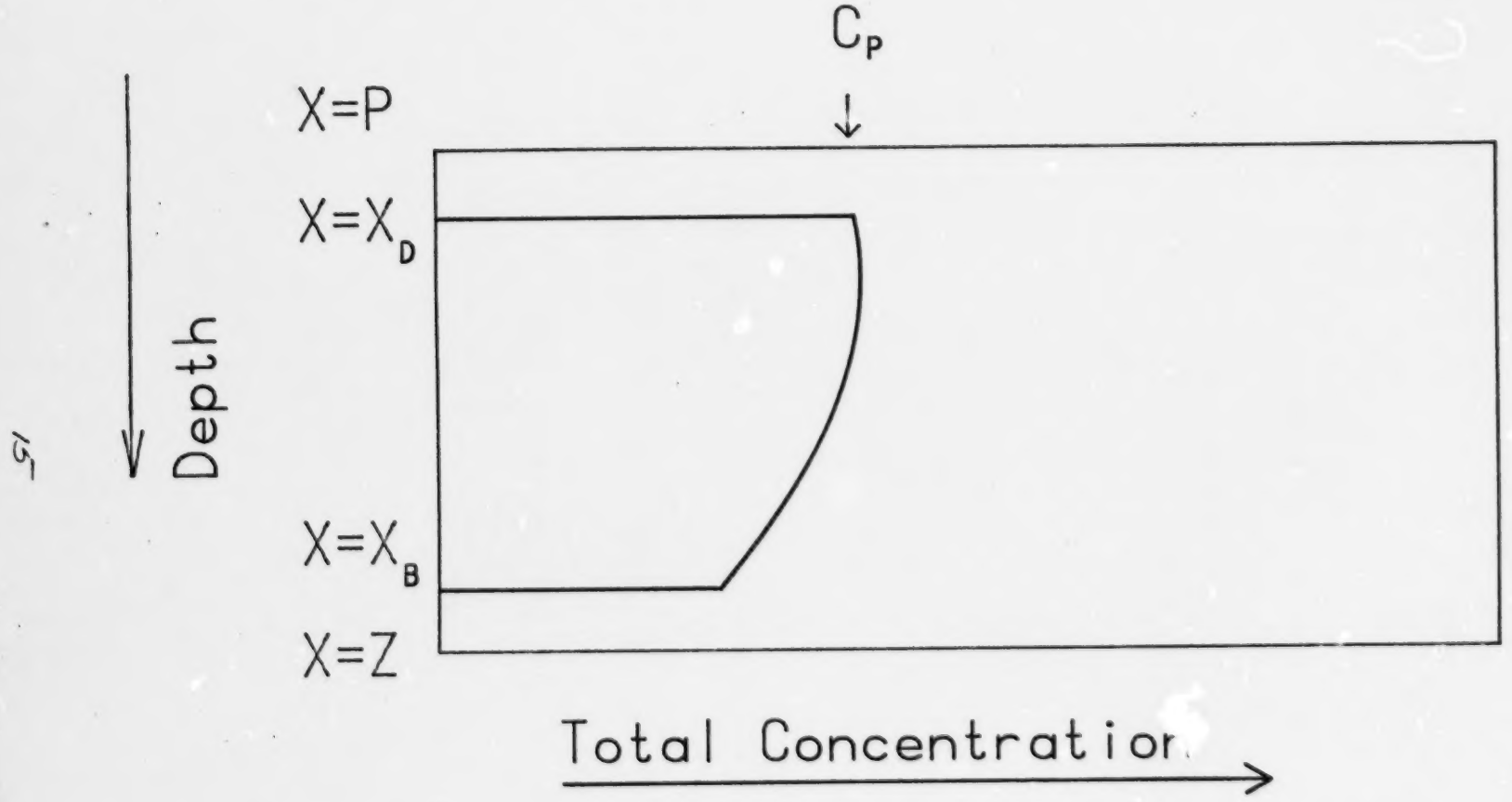

Fig. 5. Lower Treatment Zone Mass Balance

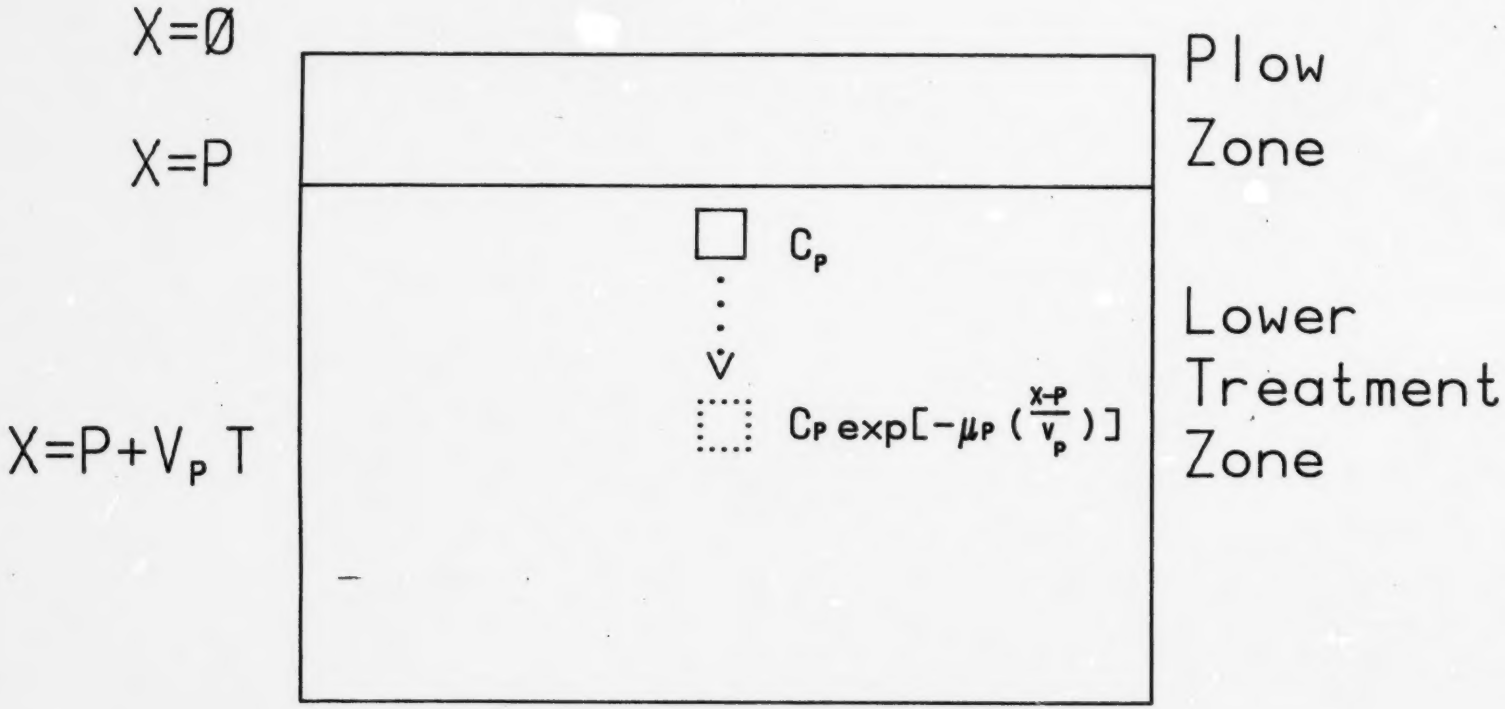

Fig. 6. Lower Treatment Zone Aqueous Concentration

where X_B = the depth of the leading edge of the pollutant slug in the lower treatment zone

$$X_B = t\ V_P + P \tag{29}$$

V_P = velocity of the pollutant slug (M/day)

Volatilization from Lower Treatment Zone

Volatilization from the lower treatment zone is handled in the same way as volatilization from the plow zone. The only difference is that volatilization can not occur until the "wet/dry" zone has broken through the plow zone at time t_{BRK} . Thus an expression for the total amount of pollutant volatilized from the treatment zone is given by equation (26).

$$\text{volatile} = \int_{t<t_{BRK}}^{t} J\,dt \tag{30}$$

Degradation in the Lower Treatment Zone

Pollutants in the lower treatment zone are assumed to degrade by first-order kinetics at the same rate that occurs in the plow zone. That being the case, an expression for the total amount of pollutant degraded in the lower treatment zone can be developed as is shown in equation (27).

$$\text{degradation} = \int_{0}^{t} (\text{accumulation})\ dt \tag{31}$$

Lower Treatment Zone Equation

Now the material balance can be completed and an expression derived which determines the location of the "wet/dry" interface when it is in the lower treatment zone. This location in turn can be used to evaluate all of the mass balance terms such as volatilization, degradation, etc. To do this, equation (27), (28), (30), and (31) combined and then differentiated to yield the differential equation shown in equation (32). This equation defines the position of the "wet/dry" interface in the lower treatment zone.

$$\frac{dX_D}{dt} = V_P + \frac{A\,V_P}{(D_S\delta + D_A X_D)} \qquad (32)$$

This differential equation can be solved by simple integration using the initial condition that the location of the interface is at the plow zone depth at the breakthrough time, t_{BRK}. This solution is shown below:

$$t = t_{BRK} + \left(\frac{X_D - P}{V_P}\right) - \left(\frac{A}{V_P D_A}\right) \ln\left[\frac{D_S\delta + A + D_A X_P}{D_S\delta + A + D_A P}\right] \qquad (33)$$

The equations developed in this paper assume a single application of waste. However, it is anticipated that the basic approach can be easily modified to cover the use of repetitive application.

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